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(56) Documents cited

J. Marshall et al, 1987, British Crop Protection  
Conference Weeds (I), page 233-240

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(54) Herbicidal agents based on metamitron/ethofumesate/phenmedipham/desmedipham

(57) Finished formulations of the known herbicidal active compounds metamitron (I) + ethofumesate (II) +

- (A) phenmedipham (III) or
- (B) phenmedipham (III) and desmedipham (IV) or
- (C) desmedipham (IV).

preferably solid formulations such as water-dispersible powders or water-dispersible granules, the ratio by weight of the active compounds (I):(II):(III) or (IV) being (1):(0.05 to 1), of the active compounds (I):(II):(III):(IV) being (1):(0.05 to 1):(0.05 to 1):(0.05 to 1), and the total active compound content in each case being between 20 and 75 % by weight.

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HERBICIDAL AGENTS BASED ON A COMBINATION OF  
METAMITRON/ETHOFUMESATE/PHENMEDIPHAM/DESMEDIPHAM

The invention relates to new finished formulations of the known herbicidal active substances metamitron + ethofume-  
5 sate + (A) phenmedipham, or (B) phenmedipham + desmedipham or (C) desmedipham, preferably solid formulations such as water-dispersible powders (WP) and water-dispersible granules (WG), and their use as herbicides, in particular as selective beet herbicides.

Mixtures of these active compounds have previously been described, ditto tank mixes of a finished formulation of ethofumesate + phenmedipham with metamitron (cf. 10 J. Marshall et al, 1987, British Crop Protection Conference Weeds (1), page 233-240), which have proved suitable in practice for selective combating of weeds in beet cultures. However, the disadvantage of these tank 15 mixes is that the user has to mix the liquid finished formulation of ethofumesate + phenmedipham [tradename: \*BETANAL-TANDEM, manufactured by Schering AG; an emulsion concentrate (EC) containing 94 g/l of ethofumesate and 97 g/l of phenmedipham] or ethofumesate + phenmedipham + 20 desmedipham [tradename: \*BETANAL-PROGRESS, manufactured by Schering AG, an emulsion concentrate (EC) containing 128 g/l of ethofumesate, 62 g/l of phenmedipham and 16 g/l of desmedipham] and the solid metamitron prepara- 25 tion [tradename: \*GOLPIX, manufactured by Bayer AG; WG, 70 %] when making up the spray mixture.

A finished formulation with a combination of these active

compounds would therefore be advantageous for the user. However, it was not known to date in which manner such finished preparations can be structured since particular problems were to be expected regarding the relatively low 5 melting point of ethofumesate and the incorporation of liquid additives, which might be necessary.

Surprisingly, finished formulations containing the technical-grade active compounds metamitron and ethofume-  
state and

10 (A) phenmedipham (III) and  
(B) phenmedipham (III) and desmedipham (IV) or (C)  
desmedipham (IV),

were now successfully prepared. Solid combination prepara-  
tions could be prepared, in some cases, using liquid  
15 emulsifiers. Particularly advantageous for agricultural  
practice are the new finished formulations in the form of  
water-dispersible granules (WG).

The invention therefore relates to new herbicidal agents  
in the form of finished formulations, containing a  
20 combination of the active compounds

metamitron (I) and ethofumesate (II) and

(A) phenmedipham (III) or  
(B) phenmedipham (III) and desmedipham (IV) or  
(C) desmedipham (IV),

25 preferably in solid form such as water-dispersible  
powders (WP), or in the form of water-dispersible  
granules (WG), as a mixture with formulation auxiliaries,  
the ratio by weight of the active compounds

(I):(II):(III) according to the combination (A) being (1):(0.05 to 1):(0.05 to 1), preferably (1):(0.1 to 0.4):(0.1 to 0.4), and particularly preferably (1):(0.1 to 0.35):(0.1 to 0.3), and the ratio by weight of the active substances (I):(II):(III):(IV) according to combination (B) being (1):(0.05 to 1):(0.05 to 1):(0.05 to 1), preferably (1):(0.1 to 0.4):(0.1 to 0.4):(0.1 to 0.4), and particularly preferably (1):(0.1 to 0.4):(0.1 to 0.35):(0.1 to 0.25),

the ratio by weight of the active compounds (I):(II):(IV) according to combination (C) being (1):(0.05 to 1):(0.05 to 1), preferably (1):(0.1 to 0.4):(0.1 to 0.4), and particularly preferably (1):(0.1 to 0.4):(0.1 to 0.3), the total active substance compound, both in the case of combination (A), that is to say (I)+(II)+(III) and for the combinations (B), that is to say (I)+(II)+(III)+(IV), and (C), that is to say (I)+(II)+(IV) being between 20 and 75 % by weight, preferably between 30 and 70 % by weight.

Preferred solid formulations are formulations such as water-dispersible powders (WP) and water-dispersible granules (WG). Particularly preferred solid formulations are water-dispersible granules.

As has been found, the WP formulations can be prepared in a surprisingly simple manner by mixing the active compounds with the formulation auxiliaries suitable for a WP formulation in the abovementioned ratio by weight, grinding the mixture (for example using a customary air-

jet mill), followed by homogenising by remixing.

The WG formulations are obtained by

- 5 (a) first preparing a premix from the active compounds (I), (II) and (III) or (I), (II), (III) and (IV) or (I), (II) and (IV) - in the abovementioned ratios by weight - and the formulation auxiliaries which are suitable for a WG formulation by mixing, grinding (expeditiently using a customary air-jet mill), followed by remixing,
- 10 (b) then treating this premix with water in a fluidised-bed granulator in a customary manner, followed by drying at an inlet air temperature of 50-90°C to a product temperature of 30-60°C, and
- 15 (c) separating the desired granules (having particle sizes between 200 and 1500 µm) by sieving, the too small particles (<200 µm) and the too large particles (>1500 µm) being separated off.

20 As has furthermore been found, a particular - continuous - embodiment of the last-described process for the preparation of the WG formulations according to the invention consists in

- preparing a highly-concentrated suspension from the premix described above under (a) by adding about the same amount by weight of water with vigorous

stirring,

- then feeding this suspension to a special granulation apparatus (as described in the - corresponding - patent documents EP-A-0,163,863 or DE-A1-3,413,200)
- and continuously discharging the product formed, at a product temperature of 30-60°C and an inlet air temperature of about 100-125°C.

10 The resulting product which, by virtue of the apparatus, is highly uniform (granules having a particle size of about 500  $\mu\text{m}$ ) needs no further sieving.

Each of the active compounds are employed in the form of the technical-grade active compounds, for which the following melting points (m.p.) were determined:

15 metamitron (I) - m.p. 166°C  
[= 3-methyl-4-amino-6-phenyl-1,2,4-triazin-5(4H)-one];

20 ethofumesate (II) - m.p. 69°C  
[= 2-ethoxy-2,3-dihydro-3,3-dimethyl-5-benzofuranyl methanesulfonate];

phenmedipham (III) - m.p. 144°C  
[= 3-methoxycarbonylaminophenyl-N-(3'-methylphenyl)- carbamate].

desmedipham (IV) - m.p. 120°C  
[= 3-ethoxycarbonylaminophenyl-N-phenyl-carbamate].

5 All the relevant technical data of the active compounds can be seen from the specialist literature [cf., for example, The Pesticide Manual, 8th ed., published by The British Crop Protection Council, 1987, pages 353-354 in the case of (II), page 536 in the case of (I), pages 652-653 in the case of (III) and pages 242-243 in the case of (IV)].

10 The formulation auxiliaries required are certain carriers, dispersants and, if necessary, certain emulsifiers or wetting agents.

15 Suitable carriers are ground synthetic minerals such as aluminium oxide, silicates or silicic acids in connection with ground natural minerals such as kaolins, clays, quartz or attapulgite. In the case of the silicic acids, absorption or precipitation silicic acids have proved particularly useful.

20 Preferred dispersing agents used are ligninsulphonates or alkylaryl sulphonates.

25 Preferred emulsifiers which were used and which were effective as additives were polyoxyethylene alkyl ethers, silicone surfactants or polyols, and examples of wetting agents which can be used are condensation products of ethylene oxide with phenol. Condensation products of

ethylene oxide with phenol can also be used as emulsifiers.

All formulation auxiliaries mentioned are commercially available products.

5 The WP formulations according to the invention (combination (A) or (C)) preferably have the following composition:

per part by weight of metamitron (I):

0.1 - 0.4 parts by weight of ethofumesate (II),

10 0.1 - 0.4 parts by weight of phenmedipham (III), or

0.1 - 0.4 parts by weight of desmedipham (IV),

0.05 - 0.2 parts by weight of dispersant,

0.0 - 0.3 parts by weight of emulsifier,

0.0 - 0.1 parts by weight of wetting agent,

15 0.1 - 0.3 parts by weight of silica and

0.05 - 0.2 parts by weight of kaolin.

The WP formulations according to the invention (combination (A)) particularly preferably have the following composition:

20 per part by weight of metamitron (I):

0.1 - 0.35 parts by weight of ethofumesate (II),

0.1 - 0.3 parts by weight of phenmedipham (III),

0.05 - 0.2 parts by weight of dispersant,

0.0 - 0.3 parts by weight of emulsifier,

25 0.0 - 0.1 parts by weight of wetting agent,

0.1 - 0.3 parts by weight of silica and  
0.05 - 0.2 parts by weight of kaolin.

The WP formulations according to the invention (combination (C)) particularly preferably have the following  
5 composition:

per part by weight of metamitron (I):  
0.1 - 0.4 parts by weight of ethofumesate (II),  
0.1 - 0.3 parts by weight of desmedipharm (IV),  
0.05 - 0.2 parts by weight of dispersant,  
10 0.0 - 0.3 parts by weight of emulsifier,  
0.0 - 0.1 parts by weight of wetting agent,  
0.1 - 0.3 parts by weight of silica and  
0.05 - 0.2 parts by weight of kaolin.

The WP formulations according to the invention (combination (B)) preferably have the following  
15 composition:

per part by weight of metamitron (I):  
0.1 - 0.4 parts by weight of ethofumesate (II),  
0.1 - 0.4 parts by weight of phenmedipharm (III),  
20 0.1 - 0.4 parts by weight of desmedipharm (IV),  
0.05 - 0.2 parts by weight of dispersant,  
0.0 - 0.3 parts by weight of emulsifier,  
0.0 - 0.1 parts by weight of wetting agent,  
0.1 - 0.3 parts by weight of silica and  
25 0.05 - 0.2 parts by weight of kaolin.

The WP formulations according to the invention (combination (B)) particularly preferably have the following composition:

per part by weight of metamitron (I):

- 5 0.1 - 0.4 parts by weight of ethofumesate (II),
- 0.1 - 0.35 parts by weight of phenmedipham (III),
- 0.1 - 0.25 parts by weight of desmedipham (IV),
- 0.05 - 0.2 parts by weight of dispersant,
- 0.0 - 0.3 parts by weight of emulsifier,
- 10 0.0 - 0.1 parts by weight of wetting agent,
- 0.1 - 0.3 parts by weight of silica and
- 0.05 - 0.2 parts by weight of kaolin.

The WG formulations according to the invention (combination (A) or (C)) preferably have the following composition:

per part by weight of metamitron (I):

- 0.1 - 0.4 parts by weight of ethofumesate (I),
- 0.1 - 0.4 parts by weight of phenmedipham (III), or
- 0.1 - 0.4 parts by weight of desmedipham (IV),
- 20 0.2 - 0.5 parts by weight of dispersant,
- 0.0 - 0.3 parts by weight of emulsifier,
- 0.1 - 0.3 parts by weight of silica and
- 0.0 - 0.2 parts by weight of kaolin.

The WG formulations according to the invention (combination (A)) particularly preferably have the following composition:

per part by weight of metamitron (I):

0.1 - 0.35 parts by weight of ethofumesate (II),

0.1 - 0.3 parts by weight of phenmedipham (III),

0.2 - 0.5 parts by weight of dispersant,

5 0.0 - 0.3 parts by weight of emulsifier,

0.1 - 0.3 parts by weight of silica and

0.0 - 0.2 parts by weight of kaolin.

The WG formulations according to the invention (combination (C)) particularly preferably have the following  
10 composition:

per part by weight of metamitron (I):

0.1 - 0.4 parts by weight of ethofumesate (II),

0.1 - 0.3 parts by weight of desmedipham (IV),

0.2 - 0.5 parts by weight of dispersant,

15 0.0 - 0.3 parts by weight of emulsifier,

0.1 - 0.3 parts by weight of silica and

0.0 - 0.2 parts by weight of kaolin.

The WG formulations according to the invention (combination (B)) preferably have the following composition:

20 per part by weight of metamitron (I):

0.1 - 0.4 parts by weight of ethofumesate (II),

0.1 - 0.4 parts by weight of phenmedipham (III),

0.1 - 0.4 parts by weight of desmedipham (IV),

0.2 - 0.5 parts by weight of dispersant,

25 0.0 - 0.3 parts by weight of emulsifier,

0.1 - 0.3 parts by weight of silica and

0.0 - 0.2 parts by weight of kaolin.

The WG formulations according to the invention (combination (B)) particularly preferably have the following composition:

5      per part by weight of metamitron (I):  
0.1 - 0.4 parts by weight of ethofumesate (II),  
0.1 - 0.35 parts by weight of phenmedipham (III),  
0.1 - 0.25 parts by weight of desmedipham (IV),  
0.2 - 0.5 parts by weight of dispersant,  
10     0.0 - 0.3 parts by weight of emulsifier,  
0.1 - 0.3 parts by weight of silica and  
0.0 - 0.2 parts by weight of kaolin.

For further details, reference is made to the preparation examples.

15     Bearing in mind the basic technical problems which had to be overcome in the preparation of the new solid finished formulations, especially the water-dispersible granules, the results achieved must be considered as surprising:

20     The preparation of a ground mixture of the active compound ethofumesate usually presents difficulties because of the low melting point of about 69°C. In an air-jet mill, this results in blocked jets or caking in the grinding chamber. To date, the active compound has only been marketed in the form of a liquid formulation.  
25     However, in the mixtures described herein, the active

compound ethofumesate in the combinations (A), (B) and (C) can be ground without problems. Above all, the grindability of the herbicide mixture is also retained when, in addition to the active compounds, a liquid emulsifier is used in the formulation, up to a content of 5 about 10 %.

In general, granulation of an active compound having a low melting point presents problems. Surprisingly, however, the premix with the active substances can be 10 granulated without particular problems. Surprisingly, the premix can also be granulated when it contains a liquid emulsifier.

The granules obtained redisperse completely, even though 15 up to about 10 % of highly-disperse silica are incorporated. This silica component usually does not completely redisperse after granulation.

Surprisingly, the same premix can be granulated by the customary processes, preferably in a powder process such as, for example, fluidised-bed granulation, or in a so-called slurry process, for example, spray drying. 20 ("Slurry" means "concentrated aqueous suspension").

Surprisingly, the (pre)mixture can also be ground and, if desired, subsequently granulated when the liquid emulsifier and the active compound metamitron (I) have 25 previously been molten together at 160°C without degradation of active compound.

Furthermore, it has been found that the finished formulations according to the invention, in particular the new WG formulations, are outstandingly suitable for selective combating of weeds, in particular in beet cultures.

5 The new finished formulations prove to be high-quality preparations which meet the requirements of practice and have a broad range of activity, for combating dicotyledon and monocotyledon harmful plants including problem weeds such as *Mercurialis annua* and *Galium aparine* in beet  
10 cultures.

Surprisingly, it has emerged in corresponding comparison trials that the WG formulations according to the invention are superior to the known tank mixes in some cases as regards their action and in some cases as regards  
15 their compatibility, and hence have additional advantages compared with the prior art.

Moreover, the new finished formulations can also be employed as selective herbicides in cultures of *Beta* beets, strawberries, mangel-wurzel, spinach and other  
20 fruit and vegetable cultures.

Other typical weeds which may be mentioned which can occur in the abovementioned cultures and which can be combated successfully with the agents according to the invention are the following:

25 Dicotyledon weeds of the genera: *Sinapis*, *Lepidium*,

5           Stellaria, Matricaria, Anthemis, Galinsoga, Chenopodium, Urtica, Senecio, Amaranthus, Portulaca, Xanthium, Convolvulus, Ipomoea, Polygonum, Sesbania, Ambrosia, Cirsium, Carduus, Sonchus, Solanum, Rorippa, Rotala, Lindernia, Lamium, Veronica, Abutilon, Emex, Datura, Viola, Galeopsis, Papaver, Centaurea, Trifolium, Ranunculus, Taraxacum.

10           Monocotyledon weeds of the genera: Echinochloa, Setaria, Panicum, Digitaria, Phleum, Poa, Festuca, Eleusine, Brachiaria, Lolium, Bromus, Avena, Cyperus, Sorghum, Agropyron, Cynodon, Monochoria, Fimbristylis, Sagittaria, Eleocharis, Scirpus, Paspalum, Ischaemum, Sphenoclea, Dactyloctenium, Agrostis, Alopecurus, Apera.

15           The application rates of active compound correspond to the amounts of active compound applied in practice when the previously known tank mixes are used, in each case based on the same unit area.

20           It is particularly important for the user in agricultural practice that the new WG formulations have substantial technical advantages compared with other formulations of the same active compounds:

25           for example, packaging is simpler (can be emptied without leaving residues and hence disposed of without problems, while the amount of packaging material is considerably reduced); the granules can be measured by volume, and there is no dust formation or splashing of the concentrate

when the spray mixtures are made up; the new solid formulations are completely free from solvents compared with the known emulsion concentrates (EC).

The action of a leaf-acting herbicidal agent can be  
5 increased by adding an emulsifier. Such an additive is  
customarily added in large amounts in a tank mix. Sur-  
prisingly, only a small amount of about 5-10 % of the  
emulsifier used in the finished formulation according to  
the invention is sufficient for obtaining an increase of  
10 action of the preparations described herein.

The preparation and use examples which follow are inten-  
ded to further illustrate the invention.

A) Preparation Examples

Examples of the preparation of the WG finished formula-  
15 tions according to the invention of metamitron & etho-  
fumesate & phenmedipham.

A premixture was prepared from the components listed in  
Table 1 below by mixing, grinding the mixture in an air-  
jet mill, followed by remixing.

20 Each of these premixtures was treated with water in a  
fluidised-bed granulator manufactured by Aeromatik  
(Strea 1) in the customary manner and subsequently dried  
to a product temperature of 40°C at an inlet air tempera-  
ture of 68°C. The too small particles (<200  $\mu\text{m}$ ) and the

too large particles ( $>1500 \mu\text{m}$ ) were subsequently sieved off from the product obtained.

When the formulations WG-3, WG-5 and WG-7 were prepared, a suspension was prepared in each case using 3.0 kg of premixture and 3.0 l of water. This suspension was fed into an apparatus described in Patent Document 5 DE-A-3,413,200 or EP-A-0,163,863. The product was continuously discharged at a product temperature of 40°C and at an inlet air temperature of 110°C. Sieving of the product obtained, granules about 500  $\mu\text{m}$  in size, was no longer necessary due to the apparatus.

In the WG formulations described in Table 1, the ratio by weight of the active compounds is

15 (I):(II):(III) = 1:0.132:0.136 in the case of  
WG 1 to 10  
(I):(II):(III) = 1:0.270:0.279 in the case of  
WG 11.

The same is also true for all use examples which follow.

Table 1: Composition of the WG formulations prepared

| Formulation No.     | Active compound <sup>1)</sup><br>(I)<br>[%] | Disper-<br>(II)<br>[%] | Silica<br>(III)<br>[%] | Emulsi-<br>fier <sup>3)</sup> ,<br>[%] | Carriers <sup>4)</sup><br>Silica<br>[%] | Kaolin<br>[%] |
|---------------------|---|------------------------|------------------------|--|---|---------------|
| WG-1                | 50.0  | 6.60                   | 6.80                   | 20.0                                   | 0.0                                     | 5.0           |
| WG-2                | 50.0  | 6.60                   | 6.80                   | 20.0                                   | 5.0                                     | 7.5           |
| WG-3                | 50.0  | 6.60                   | 6.80                   | 20.0                                   | 5.0                                     | 7.5           |
| WG-4                | 45.0  | 5.94                   | 6.12                   | 20.0                                   | 7.5                                     | 7.5           |
| WG-5                | 45.0  | 5.94                   | 6.12                   | 20.0                                   | 7.5                                     | 7.5           |
| WG-6                | 45.0  | 5.94                   | 6.12                   | 20.0                                   | 10.0                                    | 10.0          |
| WG-7                | 45.0  | 5.94                   | 6.12                   | 20.0                                   | 10.0                                    | 10.0          |
| WG-8 <sup>5)</sup>  | 45.0  | 5.94                   | 6.12                   | 20.0                                   | 10.0                                    | 10.0          |
| WG-9                | 50.0  | 6.60                   | 6.80                   | 20.0                                   | 7.0                                     | 7.0           |
| WG-10 <sup>6)</sup> | 50.0  | 6.60                   | 6.80                   | 20.0                                   | about 9.6                               | 0.0           |
| WG-11               | 23.3  | 6.30                   | 6.50                   | 15.0                                   | 5.0                                     | 38.9          |

Notes:

1) Active compound (I) = metamitron, technical grade

5

Active compound (II) = ethofumesate, technical grade

Active compound (III) = phenmedipham, technical grade

2) Dispersant: alkylaryl sulphonate

3) Emulsifier: Polyoxyethylene-(6) tridecyl ether

10 In the preparations containing an emulsifier, a 50 % premixture on silica was prepared using a customary "pulveriser".

4) Carriers: highly-disperse precipitation silica + kaolin W

15 5) The amount of the active compound metamitron (I) and the amount of emulsifier were molten together at about 160°C and the melt was cooled. The waxy composition was mixed with silica.

20 6) 60 % of emulsifier and 40 % of silica were employed as the premixture; this premixture was prepared by mixing the two components. Kaolin was not added.

B) Use Examples

Preparations used in the experiments:

(a) according to the prior art - tank mix/mixture  
comparison agent consisting of

5                     \*GOLTIX/metamitron (I), manufactured by Bayer  
                   AG, 70 % WG formulation;

                   \*TRAMAT/ethofumesate (II), manufactured by  
                   Schering AG, liquid formulation, active com-  
                   pound content 200 g/l;

10                    \*BETANAL/phenmedipham (III), manufactured by  
                   Schering AG, EC formulation, active compound  
                   content 157 g/l.

(b) according to the invention -

15                   the WG finished formulations WG-1 to WG-10 of  
                   metamitron & ethofumesate & phenmedipham which  
                   are described in the preparation examples.

Experimental set-up:

20                   Preparing the active compound preparations: the amounts  
                   required of the formulations of the preparations are  
                   weighed or measured and made into spray mixtures using  
                   water.

Post-emergence method: test plants are grown in the  
greenhouse under controlled conditions (standard soil/-

normal soil, temperature, humidity, light) up to a size of 5 to 10 cm and then treated with the herbicides in a spray cabin.

5 The concentration of the spray mixtures is so chosen that the particular amounts of active compound desired per unit area are applied at an application rate of 500 l of water/ha.

10 After the treatment, the test containers containing the test plants are kept in the greenhouse until they are evaluated. Two to three weeks after the treatment, the degree of damage to the plants is assessed as a % damage compared with untreated control plants.

The figures denote:

15 0 = no action/damage (like untreated control)  
100 = total combating/complete damage

The formulations, application rates, test plants and actions can be seen from Tables A-G which follow.

Abbreviations used in the tables:

|          |   |                        |
|----------|---|------------------------|
| a.i.     | = | active ingredient      |
| 20 BEAVA | = | Beta vulgaris (beet)   |
| AMARE    | = | Amaranthus retroflexus |
| GALAP    | = | Galium aparine         |
| MATIN    | = | Matricaria inodora     |
| MERAN    | = | Mercurialis annua      |
| POLCO    | = | Polygonum convolvulus  |
| SINAL    | = | Sinapis alba           |

Table A-1  
Post-emergence test/greenhouse (standard soil)

| Formulation*)   | Application rate<br>g/ha<br>a.i. | Test plants<br>Damage or action<br>in % | BEAVIA | AMARE |
|---|----------------------------------|---|--------|-------|
| (a) according to<br>the prior art<br><u>tank mix/-</u><br><u>mixture:</u> | 2000+264+272                     | 0                                       | 70     |       |
| metamitron<br>& ethofumesate<br>& phenmedipham                            |                                  |   |        |       |
| (b) according to<br>the invention:<br><u>WG-2</u>                         | 2000&264&272                     | 0                                       | 100    |       |
| metamitron<br>& ethofumesate<br>& phenmedipham                            |                                  |   |        |       |
| <u>WG-4</u>   | 2000&264&272                     | 0                                       | 90     |       |
| metamitron<br>& ethofumesate<br>& phenmedipham                            |                                  |   |        |       |
| <u>WG-7</u>   | 2000&264&272                     | 0                                       | 90     |       |
| metamitron<br>& ethofumesate<br>& phenmedipham                            |                                  |   |        |       |

in the case of (b), cf. in each case the preparation examples (all tables A-G).

Table A-2  
Post-emergence test/greenhouse (normal soil)

| Formulation*)   | Application rate<br>g/ha<br>a.i. | Test plants<br>BEAVA | Damage or action<br>in %<br>AMARE |
|---|----------------------------------|----------------------|-----------------------------------|
| (a) according to<br>the prior art<br>[ <u>tank mix/-</u><br><u>mixture:</u><br>metamitron<br>+ethofumesate<br>+phenmedipham | 500+66+68<br>0                   | 0                    | 80                                |
| (b) according to<br><u>the invention:</u><br><u>WG-1</u><br>metamitron<br>& ethofumesate<br>& phenmedipham                  | 500&66&68<br>0                   | 0                    | 100                               |
| <u>WG-2</u><br>metamitron<br>& ethofumesate<br>& phenmedipham   | 500&66&68<br>10                  | 100                  |                                   |

Table A-2 (continuation)  
Post-emergence test/greenhouse (normal soil)

| Formulation*  | Application<br>rate<br>g/ha<br>a.i. | Test plants<br>Damage or action<br>in %<br>BEAVA<br>AMARE |
|---|-------------------------------------|---|
| (b) according to<br>the invention:                            |                                     |   |
| <u>WG-7</u><br>metamitron<br>& ethofumesate<br>& phenmedipham | 500&66&68                           | 0<br>100  |
| <u>WG-8</u><br>metamitron<br>& ethofumesate<br>& phenmedipham | 500&66&68                           | 0<br>90   |

**Table B**  
Post-emergence test/greenhouse (normal soil)

| Formulation <sup>a</sup> )   | Application<br>rate<br>g/ha<br>a.i. | Test plants<br>Damage or action<br>in %<br>BIEAVA<br>GMLAP |
|--|-------------------------------------|--|
| (a) according to<br>the prior art<br>[tank mix/-<br>mixture:<br>metamitron<br>+ethofumesate<br>+phenmedipham | 1000+132+136                        | 10<br>80   |
| (b) according to<br>the invention:<br>WG-8<br>metamitron<br>& ethofumesate<br>& phenmedipham                 | 1000&132&136                        | 10<br>98   |

Table C  
Post-emergence test/greenhouse (standard soil)

| Formulation*)   | Application rate<br>g/ha<br>a.i. | Test plants<br>Damage or action<br>in % | MATIN<br>BEAVA |
|---|----------------------------------|---|----------------|
| (a) according to<br>the prior art<br><u>tank mix/-</u><br><u>mixture:</u><br>metamitron<br>+ethofumesate<br>+phenmedipham | 4000+528+544                     | 20<br>90                                |                |
| (b) according to<br>the invention:  |                                  |   |                |
| <u>WG-1</u><br>metamitron<br>& ethofumesate<br>& phenmedipham   | 4000&528&544                     | 10<br>100                               |                |

Table D  
Post-emergence test/greenhouse (standard soil)

| Formulation*)  | Application rate<br>g/ha<br>a.i.                               | Test plants<br>BENVA | Damage or action<br>in %<br>MERAN |
|--|--|----------------------|-----------------------------------|
| (a) according to<br>the prior art<br>[tank mix/-<br>mixture:<br>metamitron<br>+ethofumesate<br>+phenmedipham | 4000+528+544   | 20                   | 90                                |
| (b) according to<br>the invention:<br><u>WG-3</u>  | 4000&528&544<br>metamitron<br>& ethofumesate<br>& phenmedipham | 0                    | 90                                |

Table E-1  
Post-emergence test/greenhouse (standard soil)

| Formulation*  | Application rate<br>g/ha<br>a.i. | Test plants<br>Damage or action<br>in %<br>POLCO |
|---|----------------------------------|--|
| (a) according to<br>the prior art<br><u>tank mix/-</u><br><u>mixture:</u> |                                  |  |
| metamitron<br>+ethofumesate<br>+phenmedipham                              | 4000+528+544                     | 20      80                                       |
| (b) according to<br><u>the invention:</u>                                 |                                  |  |
| <u>WG-5</u><br>metamitron<br>& ethofumesate<br>& phenmedipham             | 4000&528&544                     | 0      90  |
| <u>WG-6</u><br>metamitron<br>& ethofumesate<br>& phenmedipham             | 4000&528&544                     | 10      100                                      |

Table E-2  
Post-emergence test/greenhouse (normal soil)

| Formulation <sup>a</sup>   | Application rate<br>g/ha<br>a.i. | Test plants<br>Damage or action<br>in % |     |
|--|----------------------------------|---|-----|
|  | BEAVA                            | POLCO                                   |     |
| (a) according to<br>the prior art<br>[tank mix/-<br>mixture:<br>metamitron<br>+ethofumesate<br>+phenmedipham | 20000+264+272                    | 10                                      | 90  |
| (b) according to<br>the invention:<br><br>WG-9<br>metamitron<br>& ethofumesate<br>& phenmedipham             | 20000+264+272                    | 0                                       | 100 |
| WG-10<br>metamitron<br>& ethofumesate<br>& phenmedipham  | 20000+264+272                    | 0                                       | 100 |

Table F  
Post-emergence test/greenhouse (standard soil)

| Formulation*)   | Application<br>rate<br>g/ha<br>a.i.                     | Test plants<br>Damage or action<br>in % | Test plants<br>BEAVIA | SINAL |
|---|---|---|-----------------------|-------|
| (a) according to<br>the prior art<br>[tank mix/-<br>mixture:<br>metamitron<br>+ethofumesate<br>+phenmedipharm | 4000+528+544  | 20                                      | 90                    |       |
| (b) according to<br>the invention:  | WG-5<br>metamitron<br>& ethofumesate<br>& phenmedipharm | 4000&528&544                            | 0                     | 90    |

### Patent Claims

1. Herbicidal agents in the form of finished formulations, containing a combination of the active compounds

metamitron (I) and ethofumesate (II) and  
(A) phenmedipham (III) or  
(B) phenmedipham (III) and desmedipham (IV) or  
(C) desmedipham (IV),

in a mixture with formulation auxiliaries,

10 the ratio by weight of the active compounds (I):(II):(III) according to combination (A) being (1):(0.05 to 1):(0.05 to 1),

the ratio by weight of the active compounds (I):(II):(III):(IV) according to combination (B) being (1):(0.05 to 1):(0.05 to 1):(0.05 to 1) and

the ratio by weight of the active compounds (I):(II):(IV) according to combination (C) being (1):(0.05 to 1):(0.05 to 1), and the total active compound content in the combinations (A), (B) and (C) being between 20 and 75 % by weight.

2. Herbicidal agents according to Claim 1, the ratio by weight of the active compounds (I):(II):(III) being (1):(0.1 to 0.4):(0.1 to 0.4), of the active compounds (I):(II):(III):(IV) being (1):(0.1 to

0.4):(0.1 to 0.4):(0.1 to 0.4), and of the active compounds (I):(II):(IV) being (1):(0.1 to 0.4):(0.1 to 0.4).

3. Herbicidal agents according to Claim 1, the ratio by weight of the active compounds (I):(II):(III) being (1):(0.1 to 0.35):(0.1 to 0.3), of the active compounds (I):(II):(III):(IV) being (1):(0.1 to 0.4):(0.1 to 0.35):(0.1 to 0.25), and of the active compounds (I):(II):(IV) being (1):(0.1 to 0.4):(0.1 to 0.3).

5 4. Herbicidal agents according to Claim 1, the total active compound content in the combinations (A), (B) and (C) being between 30 and 70 %.

10 5. Finished formulations according to Claim 1, in solid form.

15 6. Finished formulations according to Claim 1 or 5, carriers, dispersants and, if appropriate, an emulsifier and/or a wetting agent being employed as formulation auxiliaries.

20 7. Finished formulations according to Claim 5 in the form of water-dispersible granules.

8. Finished formulations according to Claim 5 in the form of water-dispersible powders.

9. Solid finished formulations according to Claims 5 and 8 in the form of water-dispersible powders (WP), the following formulation auxiliaries additionally being employed per part by weight of metamitron (I):

5        0.05 - 0.2 parts by weight of dispersant,  
0.0 - 0.3 parts by weight of emulsifier,  
0.0 - 0.1 parts by weight of wetting agent,  
0.1 - 0.3 parts by weight of silica and  
0.05 - 0.2 parts by weight of kaolin.

10      10. Solid finished formulations according to Claims 5 and 7 in the form of water-dispersible granules (WG), the following formulation auxiliaries additionally being employed per part by weight of metamitron (I):

15      0.2 - 0.5 parts by weight of dispersant,  
0.0 - 0.3 parts by weight of emulsifier,  
0.1 - 0.3 parts by weight of silica and  
0.0 - 0.2 parts by weight of kaolin.

20      11. Process for the preparation of finished formulations in solid form according to Claim 1, in which WP (water-dispersible powder) formulations are obtained when the active compounds are mixed with the formulation auxiliaries following the ratio by weight indicated in Claim 1, and the mixture is ground and subsequently homogenised by remixing, or in which the WG (water-dispersible granules) formulations are obtained by

5 (a) first preparing a premix from the active compounds (I), (II) and (III) or (I), (II), (III) and (IV) or (I), (II) and (IV) - according to the ratios by weight given in Claim 1 - and the formulation auxiliaries which are suitable for a WG formulation by mixing, grinding, followed by remixing,

10 (b) then treating this premix with water in a fluidised-bed granulator in a customary manner, followed by drying at an inlet air temperature of 50-90°C to a product temperature of 30-60°C, and

15 (c) separating the desired granules (having particle sizes between 200 and 1500 µm) by sieving, the too small particles (<200 µm) and the too large particles (>1500 µm) being separated off.

12. Use of the finished formulations according to Claims 1-10 as herbicides.

20 13. Use of the finished formulations according to Claim 12 as selective beet herbicides.

14. Herbicidal agent in the form of a finished formulation according to Claim 1, substantially as hereinbefore described in any one of the Preparation Examples.